Thermoelectric Figure of Merit of Strongly Correlated Superlattice Semiconductors

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We solved the Anderson Lattice Hamiltonian to get the energy bands of a strongly correlated semiconductor by using slave boson mean field theory. The transport properties were calculated in the relaxation-time approximation, and the thermoelectric figure of merit was obtained for the strongly correlated semiconductor and its superlattice structures. We found that at room temperature ZT can reach nearly 2 for the quantum wire lattice structure. We believe that it is possible to find high values of thermoelectric figure of merit from strongly correlated semiconductor superlattice systems.

For a material to be a good thermoelectric cooler, it must have a high value of the thermoelectric figure of merit Z[1], which is defined as $Z = Q^2\sigma/K$, where Q is the thermopower(Seebeck coefficient), σ is the electrical conductivity, and K the thermal conductivity. The best thermoelectric material now known is Bi_2Te_3, which has $ZT \approx 1$ at room temperature[1]. No materials are found at lower temperature with ZT larger than 1. Recently, much work has been done on strongly correlated semiconductors (also termed as Kondo insulators), and some authors suggested that this class of materials may be good candidates for thermoelectric materials[2–4]. Some experiments have been carried out to try to find good thermoelectric materials from strongly correlated semiconductors[2,5], however, so far there is no satisfactory result.

The strongly correlated semiconductors can be characterized as a mixed-valence semiconductor with a band gap less than 1000K[6]. The small value of the gap and its significant temperature dependence have been shown to be consistent with a band structure where the hybridization between local f or d electrons and the conduction band is strongly renormalized by many body effects due to the large on-site f or d electron Coulomb repulsion[7,8]. Near the chemical potential the band of this class of material is almost flat[4,9]. This is a close approximation of the ideal electronic structure suggested by Mahan and Sofo[3] for thermoelectric materials, where the transport distribution function is a delta function centered about 2-3 kT from the fermi energy[3].

In this paper we calculate the transport properties of a strongly correlated semiconductor with an indirect gap of approximately 600K, which is a good approximation of the condition derived by Mahan and Sofo. Some authors have argued that a superlattice system might increase the thermoelectric figure of merit[10]. Here, we also consider the superlattice structure of the strongly correlated semiconductor, because the indirect gap for them is proportional to V^2/W (where V is the hybridized matrix element and W is the band width of the conduction electrons), one may expect a wider indirect gap for a superlattice structure. Additionally, the DOS (density of states) will also be modified to influence thermoelectric behavior. We expect that these will improve the performance of the thermoelectric figure of merit.

Our calculation follows the method used by Sanchez-Castro, Bedell, and Cooper[4,9]. Here the Anderson Lattice Hamiltonian is used, which can be written as:

$$H = \sum_{k\sigma} \epsilon_k^0 c_{k\sigma}^\dagger c_{k\sigma} + \sum_{i\sigma} \epsilon_f f_{i\sigma}^\dagger f_{i\sigma} + \frac{1}{2} \sum_{i\sigma\sigma'} U f_{i\sigma}^\dagger f_{i\sigma} f_{i\sigma'}^\dagger f_{i\sigma'}$$
$$+ \frac{1}{\sqrt{N_s}} \sum_{ik\sigma} (V e^{-i\mathbf{k}\cdot\mathbf{R_i}} c_{k\sigma}^\dagger f_{i\sigma} + c.c.), \tag{1}$$

where $c_{k\sigma}^\dagger$ is a creation operator for a conduction electron with wave vector $\mathbf{k}$ located in the first Brillouin zone and with spin $s = \pm\frac{1}{2}$; $f_{i\sigma}^\dagger$ is a creation operator for a localized f electron centered at $\mathbf{R_i}$ in the ith unit cell, N_s is the number of unit cells in the crystal. We consider the case $U = \infty$, two electrons per primitive cell, and degeneracy $N = 2$. We treat the $U = \infty$ Anderson Lattice Hamiltonian using a slave boson formalism. Here $f_{i\sigma}^\dagger$ is represented as the bilinear product $f_{i\sigma}^\dagger = \widehat{f}_{i\sigma}^\dagger b_i$, where $\widehat{f}_{i\sigma}^\dagger$ is a slave fermion creation operator representing the $|f_\sigma^{(1)} >_{\mathbf{R_i}}$ configuration, and $b_i^\dagger$ is a slave boson creation operator representing the $|f_\sigma^{(0)} >_{\mathbf{R_i}}$ configuration. In terms of the slave boson operators, the $U = \infty$ Anderson lattice Hamiltonian is rewritten as:

$$H' = \sum_{k\sigma} \epsilon_k^0 c_{k\sigma}^\dagger c_{k\sigma} + \sum_{i\sigma} \epsilon_f \widehat{f}_{i\sigma}^\dagger \widehat{f}_{i\sigma}$$
$$+ \frac{1}{\sqrt{N_s}} \sum_{ik\sigma} (V e^{-ik\cdot R_i} c_{k\sigma}^\dagger b_i^\dagger \widehat{f}_{i\sigma} + c.c.)$$
$$+ \sum_i \lambda_i (\sum_\sigma \widehat{f}_{i\sigma}^\dagger \widehat{f}_{i\sigma} + b_i^\dagger b_i - 1) \tag{2}$$

where a time independent auxilliary boson field λ_i is added, which couples to the system through the last term in the Hamiltonian and enforces the constraint of no multiple occupancy of a f site. Furthermore, the mean filed approximation is applied to the slave boson Hamiltonian by replacing the boson field with expectation value over the coherent equilibrium states, namely, $r = < b_i >$ and

$\Lambda = <\lambda_i>$. Now the resulting Hamiltonian has renormalized hybridization matrix element $\widetilde{V} = rV$ and renormalized f level position $\widetilde{\epsilon}_f = \epsilon_f + \Lambda$. After changing to the Bloch representation for the f electrons given by $\widehat{f}_{k\sigma}^\dagger = \frac{1}{\sqrt{N_s}}\sum_i e^{-ik\cdot R_i}\widehat{f}_{i\sigma}^\dagger$, a canonical transformation is performed to the hybridized band creation operators as follows,

$$\left[\begin{array}{c} a_{k1\sigma}^\dagger \\ a_{k2\sigma}^\dagger \end{array}\right] = \left[\begin{array}{cc} \alpha_{k\sigma} & \beta_{k\sigma} \\ -\beta_{k\sigma} & \alpha_{k\sigma} \end{array}\right]\left[\begin{array}{c} \widehat{f}_{k\sigma}^\dagger \\ c_{k\sigma}^\dagger \end{array}\right]$$

where $a_{k1\sigma}^\dagger = \alpha_k\widehat{f}_{k\sigma}^\dagger + \beta_k c_{k\sigma}^\dagger$ and $a_{k2\sigma}^\dagger = -\beta_k\widehat{f}_{k\sigma}^\dagger + \alpha_k c_{k\sigma}^\dagger$.

$$\alpha_k^2 = \frac{1}{2}(1 + \frac{\epsilon_k^0 - \widetilde{\epsilon}_f}{E_k}) \tag{3}$$

$$\beta_k^2 = \frac{1}{2}(1 - \frac{\epsilon_k^0 - \widetilde{\epsilon}_f}{E_k}) \tag{4}$$

In terms of the hybridized band operators, the mean field Hamiltonian simplifies to:

$$H^{MF} = \sum_{kn\sigma}\epsilon_{kn}a_{kn\sigma}^\dagger a_{kn\sigma} + N_s\Lambda(r^2 - 1), \tag{5}$$

where $n = 1, 2$ is the band index and ϵ_{kn} is the hybridized band energy given by

$$\epsilon_{kn} = \frac{1}{2}(\epsilon_k^0 + \widetilde{\epsilon}_f + (-1)^n E_k), \tag{6}$$

and

$$E_k = ((\epsilon_k^0 - \widetilde{\epsilon}_f)^2 + 4r^2V^2)^{\frac{1}{2}}, \tag{7}$$

The resulting DOS are given by

$$\rho_{c\sigma}(\omega) = \frac{1}{N_s}\sum_k \delta(\omega - \frac{\widetilde{V}^2}{\omega - \widetilde{\epsilon}_{f\sigma}} - \epsilon_{k\sigma}) \tag{8}$$

$$\rho_{f\sigma}(\omega) = \frac{\widetilde{V}^2}{(\omega - \widetilde{\epsilon}_{f\sigma})^2}\rho_{c\sigma}(\omega). \tag{9}$$

The equations for determining the expectation values of the boson fields are obtained by minimizing the mean field energy with respect to r and Λ respectively. The resulting equations to determine r, Λ and the chemical potential μ are:[11,12]

$$1 - r^2 = \frac{1}{N_s}\sum_{k\sigma}(\alpha_{k\sigma}^2 n_F(\epsilon_{1\sigma}) + \beta_{k\sigma}^2 n_F(\epsilon_{k2\sigma})), \tag{10}$$

$$\Lambda = \frac{1}{N_s}\sum_{k\sigma}\frac{V^2}{E_{k\sigma}}(n_F(\epsilon_{k1\sigma}) - n_F(\epsilon_{k2\sigma})), \tag{11}$$

$$\frac{1}{N_s}\sum_{k\sigma}(n_F(\epsilon_{k1\sigma}) + n_F(\epsilon_{k2\sigma})) = 2. \tag{12}$$

where n_F is the Fermi-Dirac distribution function.

The relaxation-time approximation[13] is used in our calculation, thus the electrical conductivity σ, the thermopower Q, and the thermal conductivity κ are given by $\sigma = L_0$, $Q = -\frac{k_B}{|e|}\frac{L_1}{L_0}$, and $\kappa = \frac{k_B^2 T}{e^2}(L_2 - L_1 L_0^{-1} L_1)$, where L_m is

$$L_m = -\frac{e^2}{V}\sum_{kn\sigma}\frac{\partial n_F(\epsilon_{kn\sigma})}{\partial\epsilon_{kn\sigma}}\tau(\epsilon_{kn\sigma})\mathbf{v}_{kn\sigma}\mathbf{v}_{kn\sigma}(\frac{\epsilon_{kn\sigma} - \mu}{k_B T})^m, \tag{13}$$

For the case of a small number of impurities, the electronic relaxation time is given by

$$\frac{1}{\tau_{kn\sigma}} = \frac{\pi}{\hbar}\frac{N_{imp}}{N_s}|V_0|^2(\frac{\partial\epsilon_{kn\sigma}}{\partial\epsilon_{k\sigma}^0})^2\rho(\epsilon_{kn\sigma}), \tag{14}$$

where

$$\frac{\partial\epsilon_{kn\sigma}}{\partial\epsilon_{k\sigma}^0} = \beta_k^2(\alpha_k^2) \tag{15}$$

for $n = 1(2)$ and N_{imp} is the total number of impurities. We have assumed a value of $(N_{imp}/N_s)V_0^2 = 0.09eV^2$ for the impurity potential so that the electrical conductivity is of the same order as the material FeSi.

Now we calculate the thermoelectric figure of merit for bulk material. At first, the dispersion relation of the conduction band is assumed to be a tight-binding band expressed as following:

$$\epsilon_{k\sigma}^0 = \frac{W}{6}(cos(k_x a) + cos(k_y a) + cos(k_z a)), \tag{16}$$

To perform our calculation, we consider a cubic lattice with a lattice constant $a^3 = 83\mathring{A}^3$, $W = 5.0eV$, $V^2 = 0.4eV^2$, and $\epsilon_f = 0.67eV$ below the conduction Fermi energy, so that the indirect gap is $610K$ at $T = 0K$.

In Fig.1 the dimensionless quantity ZT as a function of temperature is shown. We find that ZT is no higher than 0.02, and it is similar to the measurement on FeSi.[2]
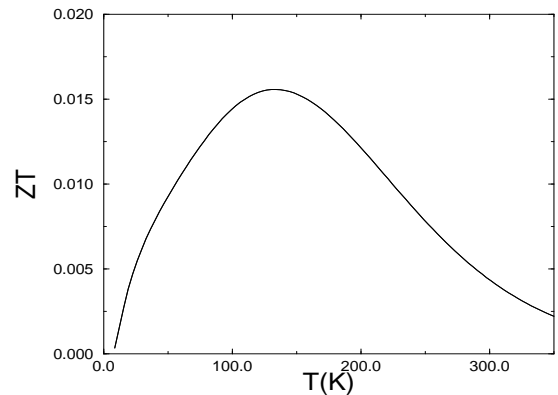
FIG. 1. The temperature dependence of the dimensionless quantity ZT for bulk material in which the conduction band is a tight-binding band

However, because the electrons and holes are almost evenly distributed when a tight-binding model is considered, and the contributions to thermopower from holes and electrons are opposite, one may expect an increase of the thermopower Q, hence ZT, if a material has such a conduction band that makes the hybridized band more different for holes and electrons respectively. Thus we replace the tight-binding band with a nearly parabolic band in our afterwards calculation, and we will pay more attention on details of this case.

The figure of merit Z has been calculated for (i) a three dimensional (3D) bulk material, (ii) a 2D multi-layered superlattice, and (iii) a 1D quantum wire lattice. It is assumed that conduction band is a nearly parabolic band. For a suitably fabricated superlattice, the conduction electrons are confined to move within 2D quantum wells or within 1D quantum wire, they occupy only the lowest subband of the quantum well or quantum line, and it is approximated that there is no tunneling between layers or lines. Thus the dispersion relation of conduction electrons in 3D is chosen to be

$$\epsilon_k^0 = \epsilon_0 + \frac{W}{3(\frac{\pi}{a})^2}[f(k_x) + f(k_y) + f(k_z)] \qquad (17)$$

where

$$f(k) = \frac{1}{2}(k^2 + (\frac{2\pi}{a} - k)^2) - [(\frac{(k^2 - (\frac{2\pi}{a} - k)^2)}{2})^2 + V_0]^{\frac{1}{2}} \qquad (18)$$

and we let $W = 6.0eV$, $V_0 = 0.1(\frac{3(\frac{\pi}{a})^2}{W})^2 eV^2$. In the 2D case, the dispersion relation becomes:

$$\epsilon_k^0 = \epsilon_0 + \frac{W}{3(\frac{\pi}{a})^2}[f(k_x) + f(k_y)] \qquad (19)$$

and in the 1D case , the dispersion relation as:

$$\epsilon_k^0 = \epsilon_0 + \frac{W}{3(\frac{\pi}{a})^2}f(k_x) \qquad (20)$$

where ϵ_0 is a constant reference energy. In our calculation, we still assume that ϵ_f is $0.67eV$ below the conduction Fermi energy so that the indirect gap at $T = 0K$ is $640K$ for 3D case.

Fig. 2 shows the transport properties verse temperature for the 3D, 2D and 1D cases, and Fig. 3 shows results of our calculation of the dimensionless quantity ZT as function of temperature. We find that at low temperature, ZT may be very large, however, it has to be noted that in our calculation, we have not included lattice thermal conductivity, which will dominate the total thermal conductivity at low temperature, thus ZT will be dramatically decreased. At room temperature, electronic thermal conductivity is larger than or comparable to lattice thermal conductivity. What's more, for superlattice system, the phonons can be scattered by the interfaces and therefore lattice thermal conductivity can be reduced. Therefore ZT in our calculation should only be affected a little bit.
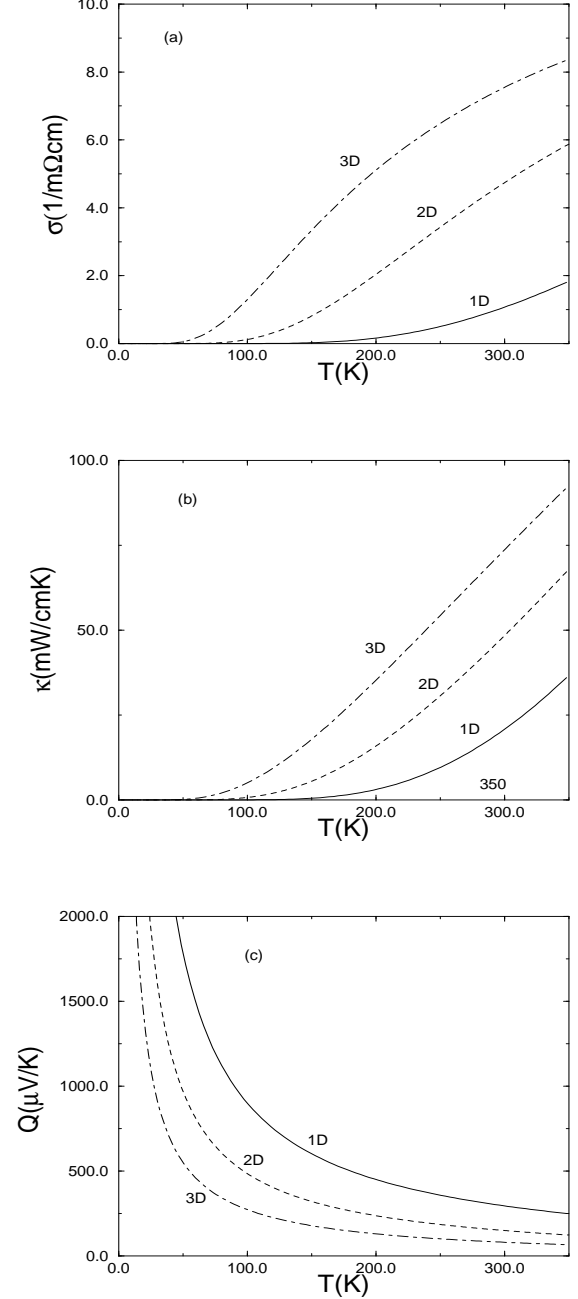

FIG. 2. The transport properties (a. electrical conductivity, b. thermal conductivity, c. thermopower) for 3D, 2D and 1D cases in which the conduction band is nearly parabolic band
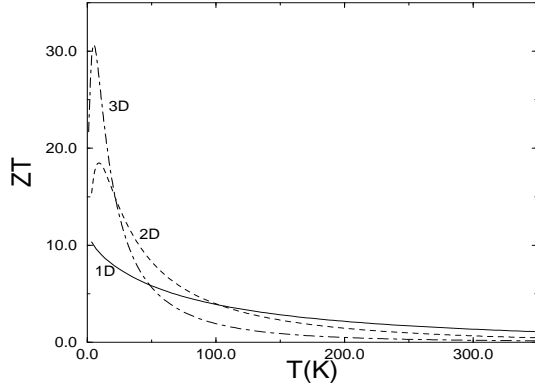
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FIG. 3. The temperature dependence of the dimensionless quantity ZT for 3D, 2D and 1D cases in which the conduction band is nearly parabolic band

In Fig. 3 we find that at room temperature, $ZT = 0.2$ for bulk material, $ZT = 0.65$ for the case of quantum well, and $ZT = 1.4$ for quantum wire. We also carried out our calculation making the indirect gap of bulk material be 1000 K, and found that ZTs at room temperature for all the three cases were increased, ZT for 1D reached 2.0, and for 2D nearly 1.5. In order to compare strongly correlated semiconductor with ordinary semiconductors, we made some calculation for ordinary intrinsic semiconductor in the cases of 3D, 2D and 1D. In these calculations, we let the indirect gap of the ordinary semiconductor be the same as the corresponding values of the strongly correlated semiconductor. At first we adjusted the effective mass of the electron band and the hole band so that in the 3D case $ZT = 0.2$ when $T = 300K$, then used these parameter to get $ZT = 0.24$ for 2D, and $ZT = 0.4$ for 1D. Comparing with the results for strongly correlated semiconductors with $ZT = 0.2$, 0.65 and 1.4 for 3D, 2D and 1D cases, we find there is an advantage in use of strongly correlated semiconductors.

Our calculation indicates that to find good thermoelectric material from strongly correlated semiconductors, the form of the conduction band is very important, and it should be a nearly parabolic band. At low temperature, unless there is some way to drop lattice thermal conductivity dramatically, ZT will not be large enough for application. At room temperature, for bulk material ZT is still very low, while the quantum wire lattice structure may have a value of ZT as large as 2. In addition, it may also be possible to increase ZT by doping as in Bi_2Te_3, where Sb or Se is added, and the up to now best p-type or n-type thermoelectric materials are achieved[1]. It is still interesting to investigate the potential application of strongly correlated semiconductor superlattice in the area of thermoelectric cooling, also further improvement by doping as in ordinary semiconductors.

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